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# Surface Hopping Excited-State Dynamics Study of the Photoisomerization of a Light-Driven Fluorene Molecular Rotary Motor

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## Supporting Information

**ABSTRACT:** We report a theoretical study of the photoisomerization step in the operating cycle of a prototypical fluorene-based molecular rotary motor (**1**). The potential energy surfaces of the ground electronic state ( $S_0$ ) and the first singlet excited state ( $S_1$ ) are explored by semiempirical quantum-chemical calculations using the orthogonalization-corrected OM2 Hamiltonian in combination with a multireference configuration interaction (MRCI) treatment. The OM2/MRCI results for the  $S_0$  and  $S_1$  minima of the relevant **1-P** and **1-M** isomers and for the corresponding  $S_0$  transition state are in good agreement with higher-level calculations, both with regard to geometries and energetics. The  $S_1$  surface is characterized at the OM2/MRCI level by locating two  $S_0$ – $S_1$  minimum-energy conical intersections and nearby points on the intersection seam and by computing energy profiles for pathways toward these MECIs. Semiclassical Tully-type trajectory surface hopping (TSH) simulations with on-the-fly OM2/MRCI calculations are carried out to study the excited-state dynamics after photoexcitation to the  $S_1$  state. Fast relaxation to the ground state is observed through the conical intersection regions, predominantly through the lowest-energy one with a strongly twisted central C=C double bond and pyramidalized central carbon atom. The excited-state lifetimes for the direct and inverse photoisomerization reactions (1.40 and 1.79 ps) and the photostationary state ratio (2.7:1) from the TSH-OM2 simulations are in good agreement with the available experimental data (ca. 1.7 ps and 3:1). Excited-state lifetimes, photostationary state ratio, and dynamical details of the TSH-OM2 simulations also agree with classical molecular dynamics simulations using a reparametrized optimized potentials for liquid simulations (OPLS) all-atom force field with ad-hoc surface hops at predefined conical intersection points. The latter approach allows for a more extensive statistical sampling.

## INTRODUCTION

A design of molecular machines, such as rotary molecular motors and photoswitches, represents a real challenge for future technology.<sup>1–10</sup> A wide variety of molecular machines ranging from single molecule switches and motors<sup>5–7,10–22</sup> to photo-mobile polymer materials<sup>23–25</sup> has been synthesized. The desired functionality, in these machines, is achieved through light-driven changes in molecular structure. This principle is used in light-driven molecular rotary motors derived from chiral overcrowded alkenes<sup>5–7,12–22</sup> in which periodic repetition of photoisomerization and thermal relaxation steps leads to a unidirectional rotation of one part of the molecule with respect to another (see e.g., Scheme 1). In these motors, clear design principles were formulated for the thermal helix inversion step, and a considerable increase in the rotation speed (ca.  $10^8$  times) has been achieved by lowering its barrier.<sup>13,14,16,17</sup> The photoisomerization step however still remained poorly understood and less amenable to judicious chemical modification. To be able to improve the design of light-driven molecular rotary motors, one needs to better understand the underlying mechanism and the effect of various factors, such as substituents, heteroatoms, and environment, on the dynamics of photorearrangement. Such

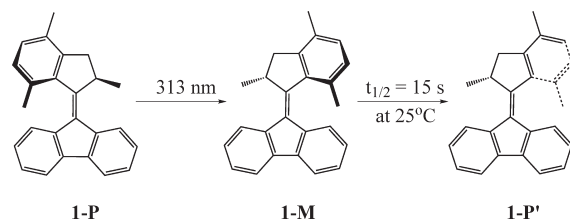
knowledge can be used not only to improve the design of synthetic molecular motors but also to gain deeper insight into the mode of action of biological molecular machines.<sup>26</sup>

These goals motivated a recent molecular dynamics (MD) study<sup>27</sup> of the rotation cycle of a particular molecular motor, 9-(2,4,7-trimethyl-2,3-dihydro-1H-inden-1-ylidene)-9H-fluorene (**1**), see Scheme 1. In this study, the potential energy surfaces (PESs) of the lowest singlet excited state ( $S_1$ ) and of the electronic ground state ( $S_0$ ) were represented by a classical force field [optimized potentials for liquid simulations (OPLS) all-atom], with a special parametrization for the excited state.<sup>27</sup> The MD-OPLS simulations started in the  $S_1$  state and returned to the  $S_0$  state via conical intersections<sup>28–30</sup> that play a crucial role in the photoisomerization of **1**. In a general sense, the mechanism of photoisomerization in **1** is basically the same as in the prototypical ethylene molecule. To reach the conical intersection, **1** needs to undergo a substantial geometric distortion that involves a twist about the central double bond and a strong pyramidalization of the central carbon atom of the fluorene moiety. Although

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Scheme 1. Isomerization Cycle of Molecular Motor 1

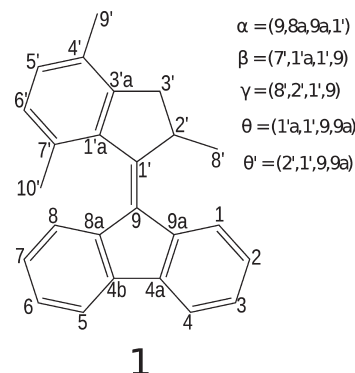


the results of ref 27 for the excited-state lifetimes, the photostationary state ratio, and the thermochemical parameters of the helix inversion step were in good agreement with experiments,<sup>16</sup> the underlying theoretical approach is based on a number of assumptions that could not be thoroughly tested. In particular, it was assumed that the population transfer occurs whenever the molecular conformation reaches a predefined geometry that corresponds to a minimum-energy conical intersection.<sup>27</sup> This assumption may artificially exaggerate the role of minimum-energy conical intersections and thus needs to be justified carefully.

A more balanced description of excited-state decay processes can be achieved with the use of semiclassical trajectory surface hopping (TSH) simulations in which the parameters governing population transfer are determined on-the-fly from quantum mechanical (QM) calculations. It is the primary purpose of the present work to carry out such TSH-QM simulations of the photoisomerization cycle of the molecular motor **1** and to obtain detailed insight into its mechanism. The results of this work should not only corroborate those of the previous study<sup>27</sup> but also provide an unbiased assessment of the role of conical intersections and avoided crossing regions for the photodynamics of **1**. The sheer size of **1** precludes the use of accurate QM methods in on-the-fly TSH-QM simulations. Therefore we have chosen an efficient semiempirical QM approach for this purpose, the OM2/graphical unitary group approach multireference configuration interaction (GUGA-MRCI) method,<sup>31–33</sup> which offers a realistic description of the ground and excited states of large molecules<sup>34,35</sup> and has recently been applied successfully in excited-state dynamics studies.<sup>36–38</sup> In the present TSH-OM2 simulations, we compute the ground- and excited-state PESs of **1** and the required nonadiabatic coupling parameters by OM2/GUGA-MRCI on-the-fly during the dynamics runs. For comparison, we report classical MD-OPLS simulations of the type of ref 27 using the conical intersection seam structures optimized with the OM2/GUGA-MRCI method. We analyze the results of the two types of simulations in the context of the experimentally observed excited-state lifetimes<sup>39</sup> and photostationary state ratios<sup>16</sup> and discuss the implications of these results for the photochemistry of sterically overcrowded alkenes.

## METHOD OF CALCULATION

To investigate the potential energy surfaces and the dynamics of **1**, semiempirical QM calculations were performed using the development version of the MNDO program.<sup>40</sup> The orthogonalization-corrected OM2 semiempirical Hamiltonian<sup>31,32</sup> and the GUGA-MRCI approach<sup>33</sup> were employed to calculate the required energies, gradients, and nonadiabatic couplings. GUGA-MRCI denotes the graphical unitary group approach to multireference configuration interaction. Three reference configurations

Scheme 2. Definition of Key Geometric Parameters of **1**

[closed-shell and single and double highest occupied–lowest unoccupied molecular orbital (HOMO–LUMO) excitations] were used to build the MRCI expansion. The self-consistent field (SCF) calculations were done in the restricted open-shell Hartree–Fock (ROHF) formalism, which provides a better description of the electronic wave function of singlet excited states than the usual restricted closed-shell Hartree–Fock approach.

The geometries of the ground- and excited-state minima were optimized for all the relevant isomers using the OM2/GUGA-MRCI method. The ground-state transition state (TS) for the first step in Scheme 1 was also optimized at the OM2/GUGA-MRCI level. The geometries of the minimum-energy  $S_0$ – $S_1$  conical intersections (MECIs) were located by using the Lagrange–Newton method with analytically calculated gradients and nonadiabatic coupling vectors.<sup>41,42</sup> The conical intersection seam in the vicinity of the located MECIs was studied by performing relaxed scans along dihedral angles corresponding to twisting about the  $C_9$ – $C_{1'}$  double bond and pyramidalization of the  $C_9$  atom (see Scheme 2).

The photoinduced nonadiabatic dynamics was investigated with Tully's surface hopping method (see refs 43–46 for further details). All relevant energies, gradients, and nonadiabatic coupling vectors were calculated on-the-fly using OM2/GUGA-MRCI. Nonadiabatic transitions at conical intersections were treated by the fewest switches algorithm,<sup>43,44,47</sup> with velocity adjustment along the nonadiabatic coupling vector after a successful hop.<sup>47</sup> The empirical decoherence correction proposed by Truhlar et al.<sup>48</sup> and Granucci et al.<sup>49</sup> was applied to improve the internal consistency of the fewest switches scheme, using the suggested value of 0.1 hartree for the empirical constant in this correction. Initial structures and velocities were obtained by Wigner sampling.<sup>50</sup> The nuclear trajectories were propagated for 2 ps with a time step of 0.1 fs. A step size of 0.001 fs was used for the propagation of the electronic motion.<sup>47</sup>

The active space in the OM2/GUGA-MRCI calculations comprised 12 electrons in 11 orbitals ( $\pi$  and  $\pi^*$ ), which was found suitable for stable dynamics simulations and for geometry optimizations along the isomerization path including the conical intersection points. To always retain the  $\pi$  orbitals in the active space, we employed a recently developed method for identifying and tracking the  $\pi$  character of orbitals.<sup>51</sup> To be included in the active space, a molecular orbital (MO) was required to have a  $\pi$ -type population exceeding 0.4 for optimizations and 0.35 for nonadiabatic dynamics (see ref 51 for further details of this approach). The chosen (12,11) active space contained the two

**Table 1.** Geometry Parameters in Å and deg of the 1-P and 1-M Conformations, the Transition State, and the Conical Intersections Obtained with OM2/GUGA-MRCI (this work) and with the RE-B3LYP/6-31G\* and SA-RE-BH&HLYP//RE-B3LYP/6-31G\* Methods (from ref 27)<sup>a</sup>

structure(state)	method	C <sub>1</sub> '–C <sub>9</sub>	α	β	γ	θ	pyr <sup>b</sup>
P(S <sub>0</sub> )	OM2/GUGA-MRCI	1.359	0.7	−39.6	102.2	168.2	1.1
	RE-B3LYP	1.368	1.7	−43.1	105.5	169.2	2.8
M(S <sub>0</sub> )	OM2/GUGA-MRCI	1.364	1.3	27.0	41.2	27.2	2.1
	RE-B3LYP	1.376	1.7	30.0	32.4	31.7	2.8
P(S <sub>1</sub> )	OM2/GUGA-MRCI	1.400	16.4	1.5	59.4	110.2	26.7
M(S <sub>1</sub> )	OM2/GUGA-MRCI	1.392	4.3	0.7	58.6	85.3	6.9
TS(S <sub>0</sub> )	OM2/GUGA-MRCI	1.438	0.2	0.2	59.1	90.0	0.3
	RE-B3LYP	1.463	0.0	5.6	66.0	90.0	0.0
CI <sub>1</sub>	OM2/GUGA-MRCI	1.420	35.5	5.7	67.2	133.5	58.0
	SA-RE-BH&HLYP//RE-B3LYP	1.490	34.0	3.8	36.8	120.0	52.7
	CASSCF(8,8)	1.423	35.5	4.9	64.9	131.0	58.1
CI <sub>2</sub>	OM2/GUGA-MRCI	1.405	−32.6	3.2	59.6	56.1	−53.6
	SA-RE-BH&HLYP//RE-B3LYP	1.472	−30.0	4.9	45.5	70.0	−47.9

<sup>a</sup> See Scheme 2 for definitions of geometry parameters for 1-P and 1-M. <sup>b</sup> Pyramidalization angle: angle between C<sub>1</sub>'–C<sub>9</sub> bond and (8a–9–9a) plane.

**Table 2.** Energies, in kcal/mol, of the Species in Table 1 Obtained from OM2/GUGA-MRCI (this work) and RE-B3LYP/6-31G\* or SA-RE-BH&HLYP/6-31G\* (from ref 27) Calculations<sup>a</sup>

state	method	P	M	TS	P(S <sub>1</sub> ) <sup>b</sup>	M(S <sub>1</sub> ) <sup>c</sup>	CI <sub>1</sub>	CI <sub>2</sub>
S <sub>0</sub>	OM2/GUGA-MRCI	0.0	2.1	35.7	40.8	37.8	62.7	66.2
	RE-B3LYP	0.0	3.5	32.1			67.6 <sup>d</sup>	70.3 <sup>d</sup>
S <sub>1</sub>	OM2/GUGA-MRCI	90.6	86.5	62.0	59.1	59.0	62.7	66.2
	SA-RE-BH&HLYP	87.6	81.7	68.0			71.2	74.0

<sup>a</sup> All values are given relative to the ground-state energy of the P conformer. <sup>b</sup> Energy minimum on the S<sub>1</sub> PES structurally closest to the 1-P conformer. <sup>c</sup> Energy minimum on the S<sub>1</sub> PES structurally closest to the 1-M conformer. <sup>d</sup> Energy obtained from SA-RE-BH&HLYP//RE-B3LYP single-point calculation.

singly occupied MOs from the ROHF treatment, the 5 highest doubly occupied  $\pi$  MOs, and the 4 lowest unoccupied  $\pi$  MOs, which was considered sufficient for capturing the major correlation effects in the OM2/GUGA-MRCI framework. For this choice, the energy gaps between the active and inactive  $\pi$  MOs were generally rather large, consistent with the fact that the (12,11) active space turned out to be quite robust during dynamics and optimizations.

To verify the molecular geometries obtained at the OM2/GUGA-MRCI level, complete active space SCF (CASSCF) calculations were undertaken for a number of the structures, using an active space with 8 electrons in 8 orbitals and the 6-31G\*\* basis set.<sup>52</sup> The CASSCF calculations were performed with the MOLPRO2008.1 package.<sup>53</sup>

The classical force field MD simulations were carried out using the Gromacs (v4.0.5) program package.<sup>54</sup> The ground- and excited-state potential energy surfaces were described by the OPLS all-atom force field,<sup>55</sup> as reparametrized in ref 27. Further details on the setup and the results of the classical MD simulations can be found in the Supporting Information. To distinguish in the following between the two types of excited-state dynamics described above, we shall use the label TSH-OM2 for the semiclassical trajectory surface hopping method with on-the-fly OM2/GUGA-MRCI calculations and the label MD-OPLS for the classical MD simulations with the reparametrized OPLS all-atom force field.

## RESULTS AND DISCUSSION

**OM2/GUGA-MRCI Calculations.** The operation cycle of the motor 1 consists of four steps (strokes) of which one photoisomerization step (power stroke) and one thermal helix inversion step are shown in Scheme 1. The geometries of the stable 1-P and the metastable 1-M conformations of 1 in the ground (S<sub>0</sub>) electronic state were optimized using the OM2/GUGA-MRCI semiempirical method. The atomic numbering scheme and the definition of the key geometric parameters of 1 are given in Scheme 2, and the results of the calculations are collected in Tables 1 and 2. Due to the increased steric repulsion, the metastable conformation 1-M is destabilized by 2.1 kcal/mol as compared to 1-P, and the central C<sub>1</sub>'–C<sub>9</sub> bond is elongated by 0.005 Å. These values are in a good agreement with the results of RE-B3LYP/6-31G\* calculations ( $\Delta E = 3.5$  kcal/mol,  $\Delta l = 0.008$  Å) for the ground-state species (see Tables 1 and 2).<sup>27</sup> The rearrangement from 1-P to 1-M occurs on the S<sub>0</sub> PES via a transition state that lies 35.7 kcal/mol (OM2/GUGA-MRCI) above the 1-P minimum, see Table 2; the corresponding RE-B3LYP/6-31G\* barrier is 32.1 kcal/mol.<sup>27</sup> The OM2/GUGA-MRCI transition state possesses an imaginary frequency of 310i cm<sup>−1</sup> associated with a twist about the C<sub>1</sub>'–C<sub>9</sub> double bond. Previously, the activation energy of the thermal helix inversion step (second step in Scheme 1) was found<sup>16,27</sup> to be 18.7 kcal/mol, which guarantees that the helix inversion is the



dominant pathway of relaxation for the metastable conformation **1-M** on the ground-state  $S_0$  PES.

The vertical excitation energies of the stable **1-P** and the metastable **1-M** conformations from OM2/GUGA-MRCI calculations are compared in Table 3 with the results of SA-RE-BH&HLYP//RE-B3LYP and TD-BH&HLYP//B3LYP calculations<sup>27</sup> and with the maxima of the absorption bands of the two conformers measured at  $-40^\circ\text{C}$  in hexane solution.<sup>16</sup> The lowest singlet  $S_1$  excited state corresponds to the excitation of one electron from the  $\pi$ -bonding to the  $\pi$ -antibonding orbital of the central  $C_1-C_9$  double bond. This state is more polar than the ground state, as indicated by the electric dipole moments of the **1-P** and **1-M** conformers in the  $S_1$  and  $S_0$  state, respectively (2.53 vs 1.30 D in **1-P** and 2.25 vs 1.20 D in **1-M**). Due to large values of the transition electric dipole moment, 7.46 D for the **1-P** conformer and 7.43 D for the **1-M** conformer, the  $S_1$  state is

**Table 3.** Excitation Energies, in eV and in nm (in parentheses), of the Stable Conformers **1-P** and **1-M** Calculated with the OM2/GUGA-MRCI, SA-RE-BH&HLYP, and TD-BH&HLYP Methods

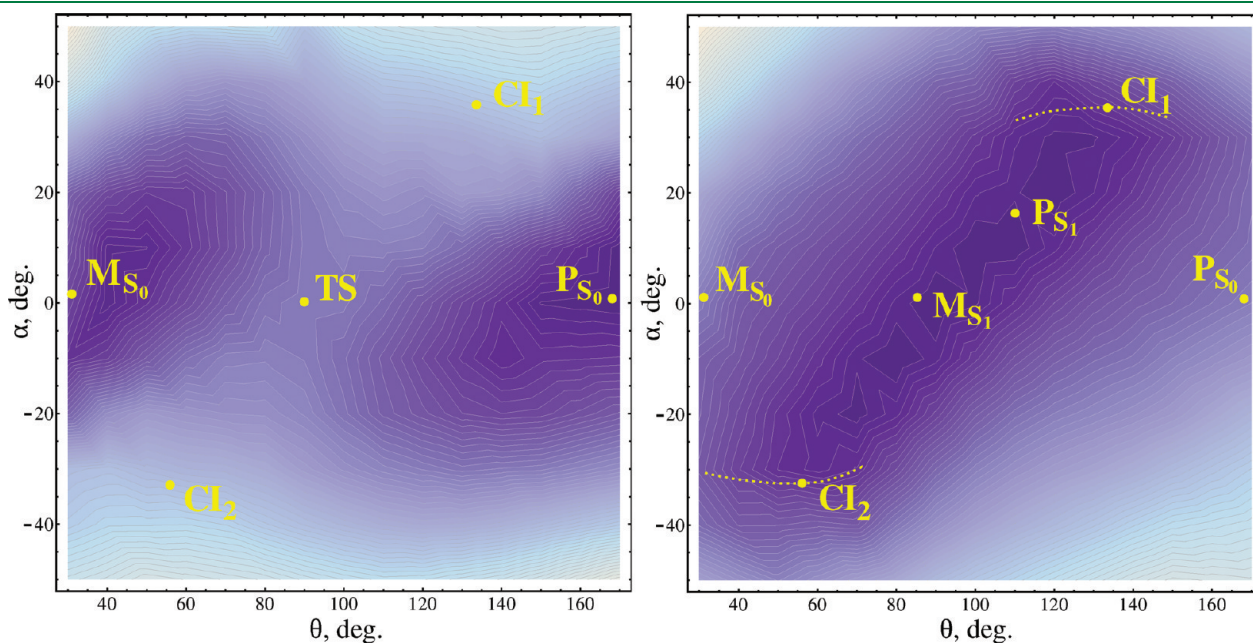
basis set	method	<b>1-P</b>	<b>1-M</b>
6-31G*	OM2/GUGA-MRCI	3.93 (315)	3.75 (331)
	SA-RE-BH&HLYP	3.80 (327)	3.40 (365)
	TD-BH&HLYP	3.78 (328)	3.39 (366)
6-311+G**	SA-RE-BH&HLYP	3.71 (334)	3.31 (375)
	TD-BH&HLYP	3.68 (337)	3.28 (378)
	expt <sup>a</sup>	3.44 (360)	3.22 (385)

<sup>a</sup> Maxima of the absorption bands measured in ref 16 in hexane solution at  $-40^\circ\text{C}$ .

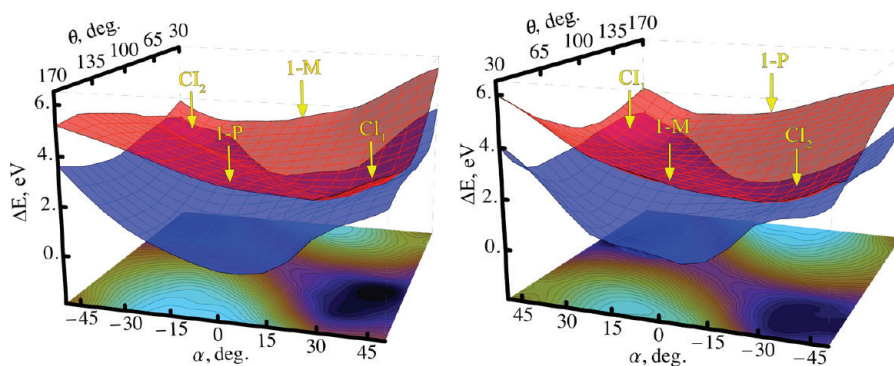
optically accessible, and the **1-P**  $\rightarrow$  **1-M** photoisomerization occurs in this state.<sup>27</sup> By contrast, the second lowest singlet  $S_2$  excited state is essentially dark. It lies about 0.4 eV above the  $S_1$  state: For the **1-P** conformer, OM2/GUGA-MRCI predicts the  $S_2$  state at 4.31 eV (288 nm) with an oscillator strength of 0.02, compared to the  $S_1$  state at 3.93 eV (315 nm) with an oscillator strength of 0.83.

For illustration purposes, the potential energy surfaces of the  $S_0$  and  $S_1$  states were obtained from relaxed scans on a two-dimensional grid of the dihedral angles  $\theta$  and  $\alpha$ . The positions of the geometric structures listed in Table 1 are shown in Figure 1 by yellow dots located at the respective values of  $\theta$  and  $\alpha$ . The  $S_1$  PES of **1** features an elongated and shallow low-energy region where two nearly degenerate stationary points can be identified. The two structures are denoted in Figure 1 and in Tables 1 and 2 as  $P(S_1)$  and  $M(S_1)$  based on their geometric proximity to one of the ground-state minima, **1-P** or **1-M**. The  $P(S_1)$  minimum lies 31.5 kcal/mol below the Franck–Condon (FC) point corresponding to the **1-P** conformation, and the  $M(S_1)$  minimum is 27.5 kcal/mol below the **1-M** FC point. These energy differences suggest that, in the  $S_1$  state, there is a substantial driving force for rotating the upper part of **1** toward twisting angles about the central  $C_1-C_9$  bond of approximately  $90^\circ$ .

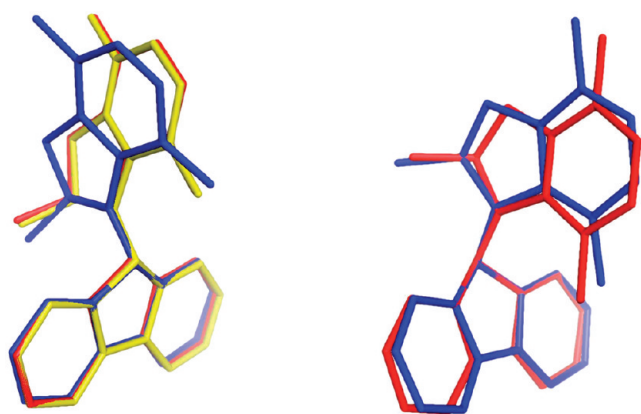
The MECI points were located at the OM2/GUGA-MRCI level using the Lagrange–Newton method with analytic non-adiabatic coupling vectors and gradient difference vectors.<sup>42</sup> The key geometry parameters of these MECI structures and their relative energies are reported in Tables 1 and 2, respectively. In Figure 1, the dihedral angles  $\alpha$  and  $\theta$  corresponding to the optimized MECI structures are shown. Note however that the energies of the optimized MECI points do not exactly match the PES contour plots in this figure (due to differences in the



**Figure 1.** Contour plots of the  $S_0$  and  $S_1$  (right and left panels, respectively) PESs of **1** obtained in OM2/GUGA-MRCI calculations (see text for details). Special points marked on the plots in yellow:  $P_{S_0}$ , minimum corresponding to the **1-P** conformation on the  $S_0$  PES;  $M_{S_0}$ , minimum corresponding to the **1-M** conformation on the  $S_0$  PES;  $P_{S_1}$ , minimum on the  $S_1$  PES geometrically closest to the **1-P** conformation;  $M_{S_1}$ , minimum on the  $S_1$  PES geometrically closest to the **1-M** conformation;  $CI_1$  and  $CI_2$ , positions of the two minimum-energy conical intersection points; and TS, transition state on the  $S_0$  PES. Dotted lines on the right panel indicate the positions of the conical intersection seam in the vicinity of MECIs as obtained with the OM2/GUGA-MRCI method.



**Figure 2.** Profiles of the  $S_0$  (blue) and  $S_1$  (red) PESs of **1** obtained from OM2/GUGA-MRCI calculations (see text for details). Left panel: view from the side of the 1-P conformation. Right panel: view from the side of the 1-M conformation. The positions of conical intersection points and Franck–Condon points are shown with yellow arrows. The contour plots below show the difference between the  $S_1$  and  $S_0$  energies.



**Figure 3.**  $CI_1$  and  $CI_2$  (left and right panels, respectively) structures as obtained from OM2/GUGA-MRCI (red), RE-BH&HLYP/6-31G\* (blue) and CASSCF(8,8)/6-31G\* (yellow) calculations (see text for details).

other geometrical parameters). The two MECIs denoted as  $CI_1$  and  $CI_2$  feature pronounced pyramidalization of the  $C_9$  atom and lie on the opposite sides of the avoided crossing region, i.e., the region in the vicinity of the TS on the  $S_0$  PES, see Figures 1 and 2. Similar conical intersection geometries were obtained previously by Kazaryan et al.<sup>27</sup> using the SA-RE-BH&HLYP/6-31G\* method. Note however that there was no search to precisely locate the MECI points in ref 27. Nevertheless, the geometries of the  $CI_1$  and  $CI_2$  points from the present work and from ref 27 closely coincide, as can be seen in Figure 3 where molecular drawings of the  $CI_1$  and  $CI_2$  geometries are superimposed. For comparison, a geometry optimized for the  $CI_1$  point using the CASSCF(8,8) method is also shown in Figure 3.

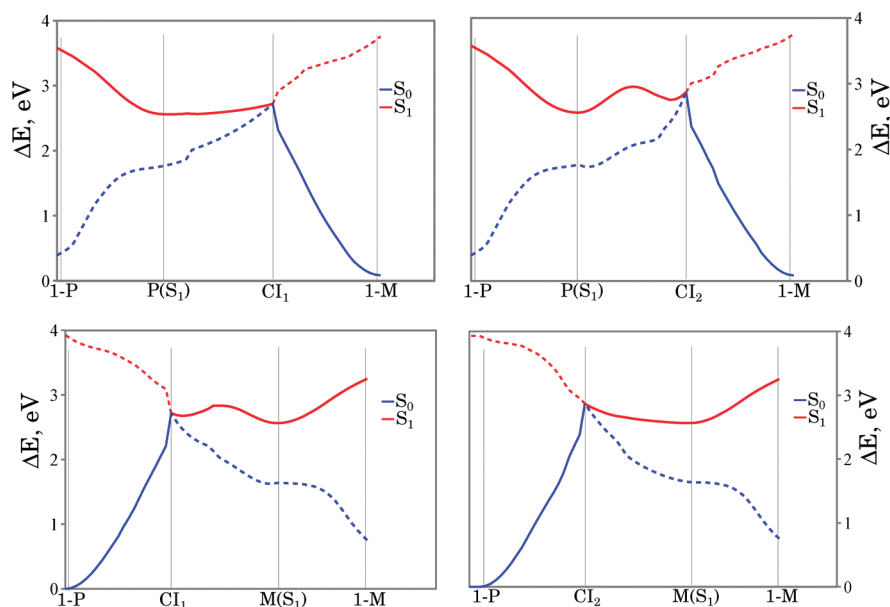
Energetically  $CI_1$  and  $CI_2$  lie 3–5 kcal/mol above the  $P_{S1}$  and  $M_{S1}$  minima on the  $S_1$  PES of **1**. The  $CI_1$  point is easily accessible from the respective FC points of the 1-P and 1-M conformations (see Figure 4), whereas there is a small barrier (ca. 3.8 kcal/mol) en route from 1-M to  $CI_1$ . This is illustrated in Figure 4 where the PES profiles are shown along pathways connecting the following points on the  $S_0$  and  $S_1$  surfaces: 1-P,  $P_{S1}$ ,  $CI_1$ , and 1-M; 1-P,  $P_{S1}$ ,  $CI_2$ , and 1-M; 1-P,  $CI_1$ ,  $M_{S1}$ , and 1-M; and 1-P,  $CI_2$ ,  $M_{S1}$ , and 1-M. These PES profiles were obtained by performing relaxed scans in these directions. During the scans, constrained geometry optimizations were carried out in the  $S_1$  state for the intervals

shown in Figure 4 with solid red lines, for fixed values of the dihedral angles  $\theta$  and  $\alpha$  that were obtained by linear interpolation between the respective structures; the  $S_0$  energies (dashed blue lines) were then computed at these optimized  $S_1$  geometries. After reaching a conical intersection, it was assumed that the system switches to the  $S_0$  ground state. Therefore constrained ground-state geometry optimizations were carried out for the intervals shown in Figure 4 with solid blue lines; the  $S_1$  energies (dashed red lines) were obtained from single-point calculations at the  $S_0$  geometries. The resulting PES profiles are presented in Figure 4.

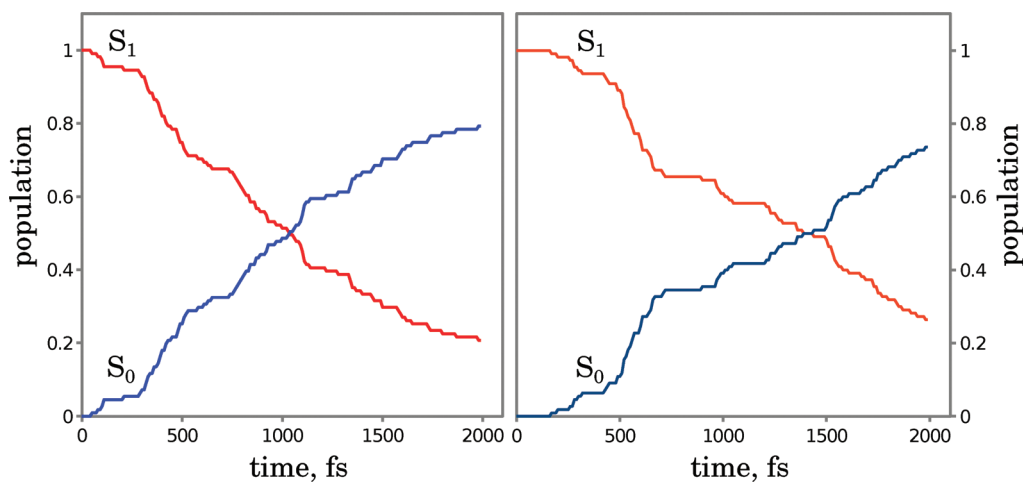
It is well-known that conical intersections play a crucial role in the radiationless relaxation of excited states.<sup>28–30</sup> The computed PES profiles of **1** suggest that the photoisomerization reaction can proceed via a barrierless pathway, and the expected excited-state lifetime should thus be quite short, of the order of 1 ps.<sup>30</sup> Specifically, for 1-P, the energy profiles for the  $S_1$  state indicate that the relaxation should predominantly occur via  $CI_1$  (see Figure 4), which is more easily accessible and also lower in energy than  $CI_2$  (see Table 2). We note that barrierless pathways toward conical intersection points were recently also reported for a molecular switch structurally similar to **1**.<sup>21,22</sup> However, even if such favorable pathways exist, the actual trajectories on the  $S_1$  PES may take somewhat different routes due to dynamical effects. To obtain more realistic information on the dynamical behavior of the system after photoexcitation and on experimental observables, such as the quantum yields of photoisomerization, one needs to carry out excited-state dynamics simulations starting from the respective FC regions.

**Molecular Dynamics Simulations.** In our semiempirical TSH-OM2 simulations, 120 trajectories were initiated for each of the 1-P  $\rightarrow$  1-M and 1-M  $\rightarrow$  1-P photoisomerization reactions. The simulations were started in the  $S_1$  state at geometries in the vicinity of the respective FC point, and the nuclear trajectories were propagated for 2 ps. The populations of the  $S_0$  and  $S_1$  states averaged over all trajectories are shown in Figure 5 for the two reactions. The  $S_1$  populations were fitted by an exponential function, which gave  $S_1$  lifetimes of 1.40 and 1.79 ps for the 1-P  $\rightarrow$  1-M and 1-M  $\rightarrow$  1-P reactions, respectively. These values are in a good agreement with the lifetimes of  $1.40 \pm 0.10$  and  $1.77 \pm 0.13$  ps, respectively, reported previously by Kazaryan et al. in their first classical MD-OPLS simulations.<sup>27</sup>

To gain more detailed structural insight into the radiationless relaxation from  $S_1$  to  $S_0$ , we inspect some characteristic angles in



**Figure 4.** PES profiles connecting the 1-P,  $P_{S1}$ ,  $CI_1$ , and 1-M structures (upper left panel), the 1-P,  $P_{S1}$ ,  $CI_2$ , and 1-M structures (upper right panel), the 1-P,  $CI_1$ ,  $M_{S1}$ , and 1-M structures (lower left panel), and the 1-P,  $CI_2$ ,  $M_{S1}$ , and 1-M structures (lower right panel) on the  $S_1$  (red) and  $S_0$  (blue) PES. The solid lines represent energies obtained from constrained geometry optimization in the respective electronic state, and the dashed lines refer to energies obtained in single-point calculations (see text for further details).



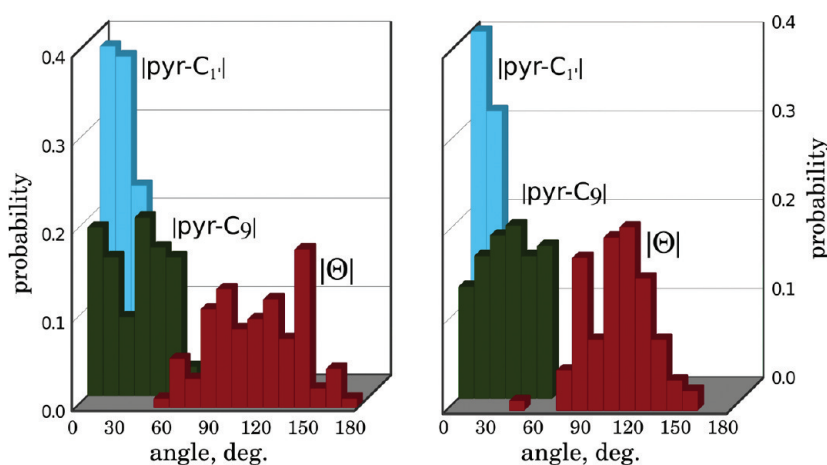
**Figure 5.** Populations of the  $S_0$  (blue) and  $S_1$  (red) states as a function of time (in fs) for the 1-P  $\rightarrow$  1-M (left panel) and 1-M  $\rightarrow$  1-P (right panel) photoisomerization reactions as obtained from the TSH-OM2 simulations.

the geometries at which surface hops occur during the TSH-OM2 simulations. The histograms in Figure 6 show the probability of surface hops as a function of the absolute values of the twisting angle  $\theta$  and the pyramidalization angles at the  $C_9$  atom and the  $C_{1'}$  atom, for all trajectories generated for the two photoisomerization reactions. Obviously, the surface hops take place predominantly at sufficiently large values of  $\theta$  (ca.  $110^\circ$  on average) and  $\text{pyr-}C_9$  (ca.  $35^\circ$  on average). The  $C_{1'}$  atom remains in a practically planar environment. It can therefore be conjectured that the surface hops occur in the vicinity of one of the MECIs found in the preceding OM2/GUGA-MRCI geometry optimizations. Indeed, both MECIs feature a rather strongly pyramidalized  $C_9$  atom and a substantial twist about the  $C_9-C_{1'}$  bond. The large average value of the dihedral angle  $\theta$  also

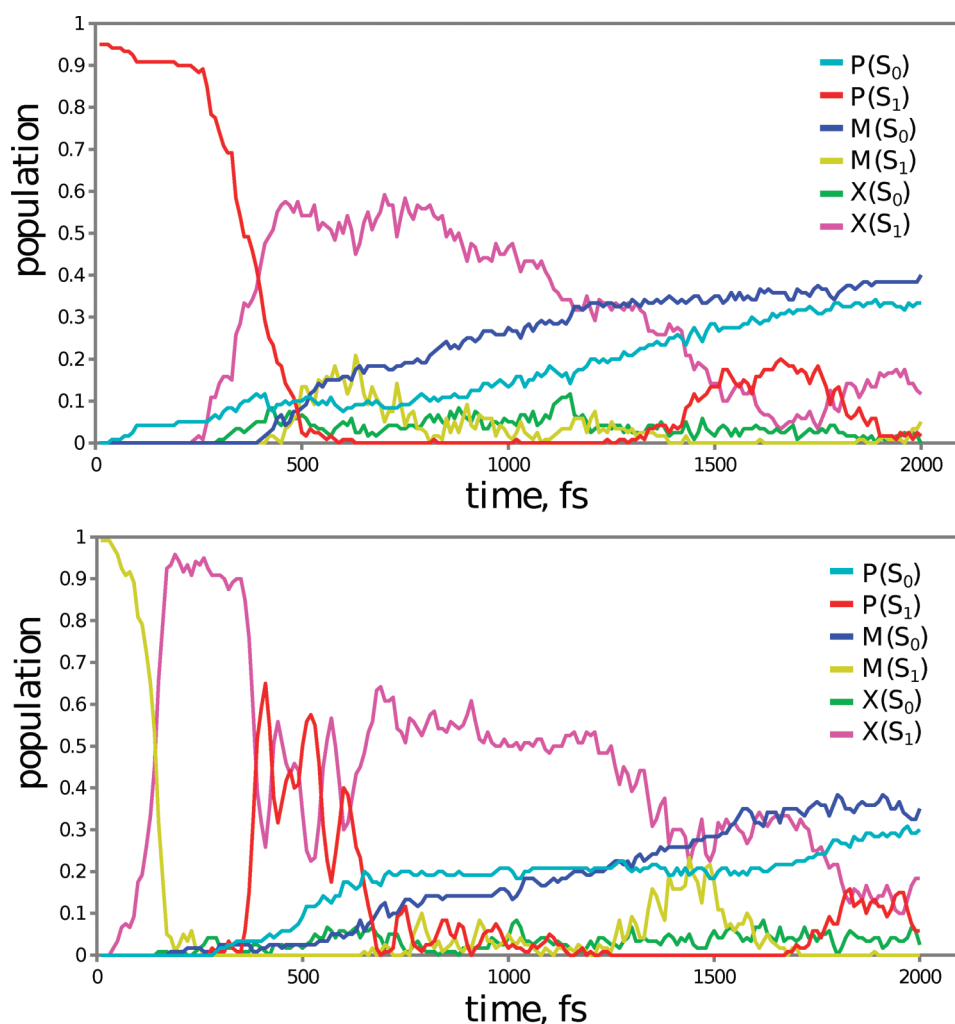
suggests that, for both photoisomerization reactions, the hops occur predominantly close to the  $CI_1$  geometry (see Table 1). These findings are consistent with the assumptions made in ref 27 when setting up the classical MD simulations.

More detailed information on the populations of the various molecular structures in the  $S_0$  and  $S_1$  states is presented in Figure 7, where the following distinctions are made in the analysis of the TSH-OM2 trajectories: The  $P(S_0)$  structure corresponds to all molecular geometries with  $\theta \geq 120^\circ$  encountered on the  $S_0$  PES. The  $P(S_1)$  structure corresponds to all geometries with  $\theta \geq 120^\circ$  encountered on the  $S_1$  PES. Analogous definitions hold for the  $M(S_0)$  and  $M(S_1)$  structures with  $\theta \leq 70^\circ$ . The  $X(S_0)$  and  $X(S_1)$  structures correspond to all intermediate geometries in the  $S_0$  and  $S_1$  states. These plots



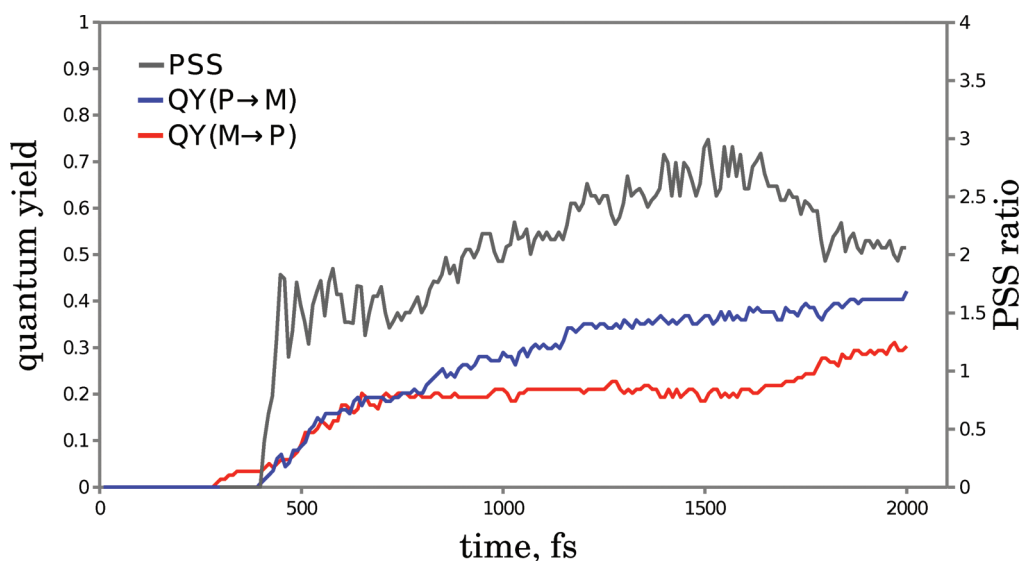


**Figure 6.** Probability of surface hops as a function of the absolute value of the angles  $\theta$  (red), pyr-C<sub>9</sub> (green), and pyr-C<sub>1'</sub> (light blue) in the TSH-OM2 trajectories for the 1-P  $\rightarrow$  1-M (left panel) and 1-M  $\rightarrow$  1-P (right panel) photoisomerization reactions. See Scheme 2 for the definition of  $\theta$  and atom labels; pyr-C<sub>9</sub> is the angle between C<sub>9</sub>–C<sub>1'</sub> bond and (8a–9–9a) plane; and pyr-C<sub>1'</sub> is the angle between C<sub>9</sub>–C<sub>1'</sub> bond and (1'a–1'–2') plane.



**Figure 7.** Time evolution of the populations of 1-P and 1-M structures in the ground  $S_0$  and excited  $S_1$  states as obtained from the TSH-OM2 simulations of the 1-P  $\rightarrow$  1-M (upper panel) and 1-M  $\rightarrow$  1-P (lower panel) photoisomerization reactions. Notation: P( $S_0$ ), 1-P isomer in the ground state; P( $S_1$ ), 1-P isomer in the excited state; M( $S_0$ ), 1-M isomer in the ground state; M( $S_1$ ), 1-M isomer in the excited state; X( $S_0$ ), intermediate molecular structure in the ground state; and X( $S_1$ ), intermediate molecular structure in the excited state (see text for details).





**Figure 8.** Quantum yields of the  $1\text{-P} \rightarrow 1\text{-M}$  (blue) and  $1\text{-M} \rightarrow 1\text{-P}$  (red) photoisomerization reactions and photostationary state ratio (gray) of the  $1\text{-P} \rightleftharpoons 1\text{-M}$  photoisomerization reaction as obtained from the TSH-OM2 simulations.

indicate that the  $1\text{-P} \rightarrow 1\text{-M}$  photoisomerization reaction is practically finished after ca. 1.5 ps, with less than 20% of the trajectories remaining in the excited state near the  $1\text{-P}$  geometry. In the case of the  $1\text{-M} \rightarrow 1\text{-P}$  reaction, ca. 30% of the trajectories remain in the excited state after ca. 1.6 ps, with the geometries intermediate between the  $1\text{-P}$  and  $1\text{-M}$  structures. This is as expected from the lifetimes evaluated for the two reactions from the data in Figure 5. We refrain from analyzing the data beyond 1.5 ps because of technical difficulties. In TSH-OM2 runs, the identification of active orbitals and the tracking of the active space may become problematic at longer simulation times, which may result in discontinuous PESs and unphysically large energy gradients.<sup>51</sup> While these problems may be partly overcome by the techniques proposed previously<sup>51</sup> and applied presently, they became unacceptably large for some of the trajectories after propagation times of more than 1.6 ps so that we prefer to focus on the TSH-OM2 results up to 1.5 ps.

In spite of these technical difficulties, we may still estimate the quantum yields of the two photoisomerization reactions and the photostationary state (PSS) ratio from Figure 7. The isomerization quantum yield of  $1\text{-P} \rightarrow 1\text{-M}$  can be obtained as the ratio of the population of the  $\text{M}(\text{S}_0)$  structures to the overall population of all structures at the start of the trajectories. The quantum yield of  $1\text{-M} \rightarrow 1\text{-P}$  can be defined analogously using the  $\text{P}(\text{S}_0)$  population. The PSS ratio of the  $1\text{-P} \rightleftharpoons 1\text{-M}$  photoisomerization reaction is then defined as the ratio of the two quantum yields. To make the calculated PSS ratio comparable to the experimentally measured one, the ratio of quantum yields was multiplied by the ratio of the optical absorption cross sections of the two conformers,  $1\text{-P}$  and  $1\text{-M}$ ,<sup>27</sup> which amounts to 1.5:1.<sup>16</sup> The so-obtained quantum yields and the PSS ratio are shown in Figure 8 as a function of simulation time. It is seen that, between 1.4 and 1.6 ps, the PSS ratio runs into a plateau and then suddenly decreases. Because this decrease is due to technical issues (see above), the final value of the PSS ratio was evaluated as the average value over the interval between 1.4 and 1.6 ps, which yields a value of 2.7:1 in a good agreement with the experimentally measured value of ca. 3:1.<sup>16</sup> Please note that the computed value refers to the gas phase, while the experimental value was determined in perdeuterated toluene.<sup>16</sup>

The simulation times that can be achieved in the TSH-OM2 simulations are rather short. To investigate whether the equilibrium parameters derived from the TSH-OM2 simulations are reliable, we used classical two-state MD-OPLS simulations, as outlined in ref 27. We initiated 1000 MD simulations in the  $1\text{-P}$  and  $1\text{-M}$  states, respectively, and the simulations were run for up to 10 ps, which allowed us to determine converged equilibrium parameters.

A detailed account of the setup and the results of the MD-OPLS simulations is given in the Supporting Information. In the present work, we extended our MD-OPLS approach of ref 27 toward a more detailed description of the CI seam, which is represented by a number of conical intersection points around the two MECIs optimized with OM2/GUGA-MRCI (see Figure 1 in this article and Table 1 in the Supporting Information). In spite of the quite different approaches, the time evolution of the total population of the  $\text{S}_0$  and the  $\text{S}_1$  states as well as the populations of individual species on the excited- and ground-state PESs of the  $1\text{-P} \rightarrow 1\text{-M}$  and  $1\text{-M} \rightarrow 1\text{-P}$  photoisomerization reactions obtained in the classical MD-OPLS simulations (see Figures 1 and 2 of the Supporting Information) closely match those from the TSH-OM2 simulations (see Figure 5). The equilibrium values of isomerization quantum yields are reached after ca. 2.5 ps (Figure 3 of Supporting Information). The value of the PSS ratio at ca. 1.5 ps is not very different from the converged value, thus justifying the approach used to calculate the PSS ratio from the results of the TSH-OM2 simulations (see Figure 8).

In summary, the dynamics of the photoisomerization obtained in the TSH-OM2 simulations is consistent with previous theoretical results<sup>27</sup> and with the available experimental data.<sup>16</sup> Comparing results of the present work with theoretical work on other photoactive molecules, the character of the lowest excited states and the mechanism of photoisomerization are qualitatively similar to what has been reported for stilbene,<sup>56–58</sup> which is not too surprising since the molecular rotor **1** contains the stilbene substructure and may be regarded as some kind of stiff stilbene.<sup>58</sup> Like in ethylene and stilbene, the relevant conical intersection is characterized by a twist about the central double bond and a strong pyramidalization at one of its two carbon

atoms. The radiationless relaxation to the ground state is an ultrafast subpicosecond process in ethylene and stilbene; it is still fast in our case, with an excited-state lifetime of 1.4 ps for **1-P**, albeit clearly slower than in ethylene and stilbene. Qualitatively, this may be due to the stiffness of **1** (arising from the annelated rings at both sides of the central double bond), which should make it more difficult to reach the conical intersection region with one strongly pyramidalized carbon atom. Finally, we note that other types of conical intersections have been reported to be involved in the photoisomerization of longer polyenes<sup>59,60</sup> and of protonated or alkylated Schiff bases that serve as retinal models<sup>61</sup> or molecular switches.<sup>21</sup>

## CONCLUSIONS

In this work, we report the results of semiclassical TSH-OM2 and classical MD-OPLS simulations of the photoisomerization step in the rotational cycle of the fluorene-based molecular rotary motor **1**. In such motors based on overcrowded alkenes, unidirectional rotation is achieved due to periodic repetition of photoisomerization and thermal relaxation steps. Hitherto, clear design principles were formulated for the thermally activated helix inversion step,<sup>13,14,16</sup> whereas the photoisomerization step remained poorly understood and less amenable to rational modification based on mechanistic understanding. A first attempt to reach such an understanding was made in ref 27 using classical two-state MD simulations for **1** with a reparametrized all-atom force field. Although the results obtained were in good agreement with experiment, the chosen ad-hoc approach was based on a number of assumptions, the validity of which could not be thoroughly tested.

The present work extends the previous study<sup>27</sup> in several ways. First, the use of the OM2/GUGA-MRCI method allows a comprehensive investigation of the excited-state dynamics. A thorough characterization of the excited-state PES of **1** has been achieved for the first time, which provides information on the topology of the conical intersection seam, the location of the energy minima, and the potential energy barriers. On the relaxed PES, the conical intersection seam is found to be easily accessible, without the need to cross potential energy barriers. This observation suggests a reinterpretation of the results of transient absorption experiments in hexane,<sup>39</sup> in which a short excited-state decay time (ca. 1.7 ps) was interpreted as relaxation time due to crossing a potential barrier. The  $S_1$  decay times obtained in the present gas-phase work from the TSH-OM2 simulations ( $\tau_{S_1} \approx 1.40\text{--}1.79$  ps), as well as those from ref 27 ( $\tau_{S_1} \approx 1.40\text{--}1.77$  ps), indicate that this relaxation time should be interpreted as excited-state lifetime. The other experimentally observed decay time, ca. 12 ps, which was associated with the transfer of population from the excited to the ground state,<sup>39</sup> may actually correspond to vibrational cooling of the “hot” ground-state species.

The semiclassical TSH-OM2 simulations clearly show that the radiationless relaxation of the excited electronic state of **1** proceeds via the conical intersection seam and that other parts of the excited state PES do not play a significant role in the mechanism of photoisomerization. Previously, this was only guessed.<sup>27</sup> The computed excited-state lifetimes for the direct, **1-P**  $\rightarrow$  **1-M**, and inverse, **1-M**  $\rightarrow$  **1-P**, photoisomerization reactions and the photostationary state ratio from the TSH-OM2 simulations are in good agreement with previous work<sup>27</sup> and with the experimental measurements.<sup>16,39</sup>

The detailed knowledge of the excited-state PES profiles and of the geometries on the conical intersection seam obtained from OM2/GUGA-MRCI calculations allowed us to amend the approach used in ref 27 and to run classical MD-OPLS simulations using an extended conical intersection seam. The excited-state lifetimes, the detailed dynamics of various conformations, and the photostationary state ratio are in good agreement with the TSH-OM2 results. After proper validation, such excited-state classical MD simulations, with predefined conical intersection structures for hopping to the ground state, can thus be useful for running very long simulations (of the order of 10 ps or more) to reach converged results or for quickly exploring the excited-state dynamics of very large molecular species. A possible application would be to study the effect of chemical modifications on the photoisomerization cycle of rotary molecular motors.

## ASSOCIATED CONTENT

**S Supporting Information.** The setup and the results of the classical MD simulations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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